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MAGNETISM AND FERROELECTRICITY

Neutron Diffraction Investigation of Structural and Magnetic States of Lithium-Doped Antiferromagnet NiO

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Abstract—The elastic neutron scattering in polycrystalline samples of the $(Ni_{1-x}Li_x)O$ solid solutions ($x < 0.1$) is investigated by neutron diffraction technique. It is shown for the first time that the doping of nickel monoxide by lithium is accompanied by the formation of vacancies in the anionic sublattice, and the vacancy concentration is equal to the lithium content in the solid solution. The neutral lithium atoms are randomly arranged over sites of the cationic sublattice with possible spatial polarization of a valence electron toward an oxygen vacancy. In the composition range studied, the diamagnetic dilution of nickel monoxide by lithium turns out to be magnetically similar to the dilution with magnesium. In both cases, the Néel temperature and the mean magnetic moment per atom linearly decrease with an increase in concentration of the diamagnetic dopant. *© 2000 MAIK "Nauka/Interperiodica".*

Nickel monoxide with crystal lattice of the NaCl type is the antiferromagnet whose magnetic structure is described by the wavevector $\mathbf{k} = (1/2, 1/2, 1/2)$ [1, 2]. This compound exhibits electrical properties characteristic of a good insulator with an electrical resistivity of about 10^{14} Ω cm [3]. It is revealed [4] that, in the case when magnesium with the same valence as the Ni^{2+} ion serves as a diamagnetic dopant, the electrical resistivity of the $(Ni_{1-x}Mg_x)O$ solid solutions obtained remains unchanged. In these solid solutions, the nickel and magnesium ions are randomly disordered over the cationic sublattice, and the anionic sublattice is completely occupied by oxygen [5–9]. The Néel temperature and the mean magnetic moment per atom linearly decrease with an increase in the concentration x, and, at $x > 0.5$, the antiferromagnetic long-range order breaks down with the formation of a state of the "cluster spin glass" type [8, 9].

Quite a different situation is observed upon diamagnetic dilution with lithium atoms. First and foremost, the doping with lithium leads to a considerable increase in the electrical conductivity of nickel monoxide, since the latter transforms from the insulator to the semiconductor with the hole conductivity [3]. Moreover, the lithium-doped nickel monoxide possesses a low value of the electronic work function, and, hence, this material can be used as a cathode in electromagnetic and electrochemical devices [10, 11]. At the same time, it was found that the cathode functions of lithium-doped nickel monoxide decrease with time due to the contamination with the Ni^{3+} ions and simple cathode dissolution. Berbenni *et al.* [11] made the assumption that such an undesirable side effect is brought about by the defectiveness of the cationic or anionic sublattices in the $(Ni_{1-x}Li_x)O$ solid solutions and attempted to reveal this feature of the sublattices with the use of thermogravimetric and X-ray diffraction analyses. Although the experimental data obtained in [10, 11] indicated the defectiveness of the anionic sublattice, the above assumption was rejected as unreliable because of insufficiently precise measurements.

The problem of the defectiveness of the sublattices in the $(Ni_{1-x}Li_x)O$ solid solutions is of particular importance in determining structural and electronic states of diamagnetic lithium atoms in the NiO lattice. Indeed, in the case of the $(Ni_{1-x}Li_x)O$ solid solutions, the small ionic radius of lithium suggests that lithium atoms can be located either in tetrahedral sites of the oxygen sublattice, when the octahedral sites have already been completely occupied by the Ni^{2+} ions, or in the octahedral sites, when the anionic sublattice is only partially occupied by oxygen atoms.

However, beginning with the work published by Goodenough *et al.* [12], the lithium-doped nickel monoxides have been considered in terms of the formula $(Ni^{2+}_{1-2x}Ni^{3+}_xLi^+_x)O$, which suggests that lithium ions occupy only octahedral sites in the anionic sublattice that is completely occupied by oxygen ions. Furthermore, Li *et al.* [13] established that the doping with lithium initially brings about the formation of the $(Ni_{1-x}Li_x)O$ solid solutions with randomly substituted sites in the cationic sublattice of the NaCl-type structure and, then, at $x = 0.5$, leads to the structural transformation from the cubic phase to the $(Ni_{0.5}Li_{0.5})O$ hexagonal phase characterized by an ordered arrangement of Li^+ and Ni^{3+} ions. According to [14, 15], the short-range order is formed even at $x = 0.3$. As a result of the structural rearrangement of atoms in the NaCl-type lattice, the magnetic ordering changes from antiferromagnetic to ferromagnetic through intermediate ferrimagnetic states at $0.3 \le x < 0.5$ [12, 15].

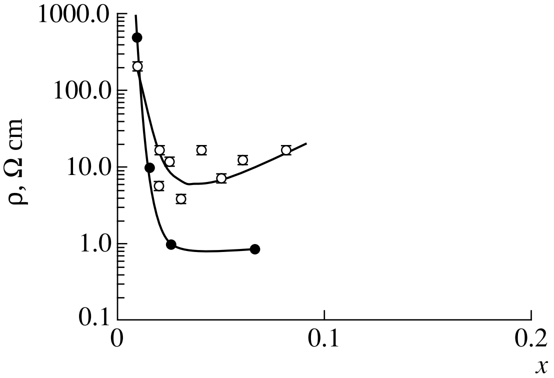

Fig. 1. Dependences of the electrical resistivity on the lithium concentration in NiO at room temperature for single crystals [3] (filled circles) and polycrystalline samples studied in this work (open circles).

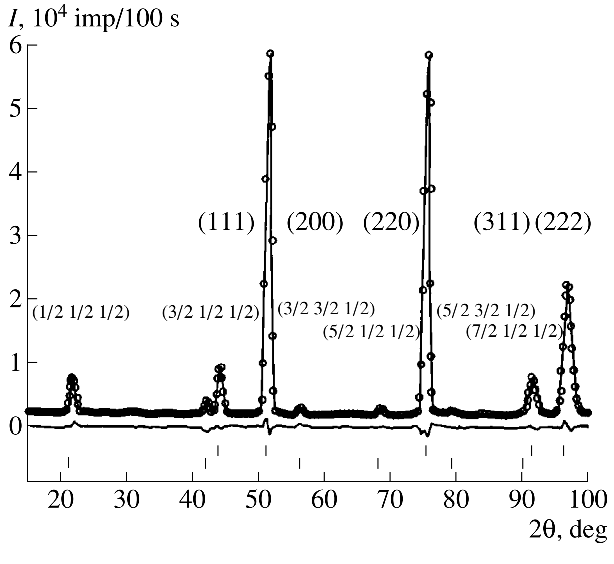

Fig. 2. Neutron diffraction pattern of the $(Ni_{1-x}Li_x)O$ solid solution at $x = 0.03$. The pattern is typical of all the studied compounds. Points are the experimental intensities, solid lines represent the intensities calculated with the assumption of an imperfect oxygen sublattice. The integer and noninteger (*hkl*) indices correspond to the nuclear and magnetic reflections, respectively.

The aim of the present work was to reveal the defectiveness of the structure of lithium-doped nickel monoxide by the neutron diffraction technique. In our case, the neutron diffraction method proved to be more sensitive to structural changes as compared to the X-ray diffraction analysis, because the nuclear-scattering amplitudes for lithium ($b_{Li} = -0.194 \times 10^{-12}$ cm), on the one hand, and nickel ($b_{Ni} = 1.03 \times 10^{-12}$ cm) and oxygen ($b_O = 0.577 \times 10^{-12}$ cm), on the other hand, are different in sign. Moreover, the neutron diffraction technique makes it possible to trace changes in both atomic and magnetic subsystems simultaneously.

1. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

For experiments, samples of NiO doped with lithium at different concentrations were prepared by the salt decomposition method. Carbonates $NiCO_3$ and Li_2CO_3 (high-purity grade) used as the initial compounds were mixed in molar ratios corresponding to the specified compositions. The mixed aqueous solutions were dried at a temperature of 120–130°C and then were calcinated at 300–800°C to the complete decomposition of salts. The materials thus prepared were carefully ground in an agate mortar, pressed into pellets, and, again, annealed at a temperature of 1200–1300°C for 6–10 h. We synthesized samples of the $(Ni_{1-x}Li_x)O$ solid solutions with the compositions x = 0.01, 0.02, 0.025, 0.03, 0.04, 0.05, 0.06, and 0.08. The values of x corresponded to the specified lithium content and were refined from the unit cell parameters. According to the X-ray diffraction analysis, all the prepared compounds exhibit crystal lattice of the NaCl type without distortions.

In addition, the quality of the prepared samples was checked by measuring the electrical resistivity at room temperature. The data obtained are displayed in Fig. 1. It can be seen that, as the lithium content in NiO increases, the electrical resistivity changes by more than thirteen orders of magnitude. Moreover, the electrical resistivity measured in this work on polycrystalline samples rather well correlates with the data obtained for single crystals in [3].

The elastic neutron-scattering measurements were carried out with the polycrystalline samples in the temperature range 77–550 K, which corresponds to the magnetically ordered state of the studied objects. All the neutron diffraction patterns were obtained in the range 2θ = 10°–110° (λ = 1.81 Å) on a diffractometer installed at a horizontal channel of an IVV-2M reactor (Zarechnyĭ, Russia). The numerical processing of the elastic neutron-scattering data was based on the fitting of calculated and experimental intensities. The calculations were performed with the Rietveld method included in the FULLPROF program [16].

2. RESULTS

Figure 2 demonstrates the neutron diffraction pattern of the $(Ni_{1-x}Li_x)O$ solid solution at the concentration $x = 0.03$. Similar neutron diffraction patterns are observed for the other compositions. Two types of reflections clearly manifest themselves in the elastic neutron-scattering pattern of the studied compounds. These reflections are indexed on the cubic NaCl-type unit cell with the integer and non-integer (*hkl*) values and correspond to nuclear and magnetic reflections, respectively. The latter reflections with the original (1/2 1/2 1/2) reflection indicate the antiferromagnetic ordering of the NiO type. The Néel temperatures of the studied compounds were determined from the temperature dependences of the intensity of the original reflection. A number of these dependences are depicted in Fig. 3. As can be seen, the Néel temperature that corresponds to the zero intensity of this reflection decreases with an increase in the lithium content in NiO. The concentration dependences of the Néel temperatures for the $(Ni_{1-x}Mg_x)O$ and $(Ni_{1-x}Li_x)O$ solid solutions are compared in Fig. 4. It is clear that there is a close correlation between both dependences. These results are in good agreement with the data on the temperature dependence of the magnetic susceptibility [17].

The required data on the other parameters of the atomic and magnetic subsystems of the $(Ni_{1-x}Li_x)O$ solid solutions were obtained by the numerical processing of the neutron diffraction patterns with the use of the FULLPROF program package. In the numerical processing of the neutron diffraction patterns, the variable parameters were three main parameters of the atomic subsystem, namely, the unit cell parameter $a(x)$, the site occupancy of the metal atoms P_{Me}, and the occupancy of the oxygen atoms P_O. The mean magnetic moment $\langle\mu\rangle$ per atom of the antiferromagnetic lattice served as the characteristic parameter of the magnetic subsystem. All the calculations were performed under the assumption that the magnetic structure of the $(Ni_{1-x}Li_x)O$ solid solutions at $x \le 0.1$ is described by the wavevector $\mathbf{k} = (1/2, 1/2, 1/2)$.

The results of numerical calculations unambiguously indicate that, for the $(Ni_{1-x}Li_x)O$ solid solutions, the best discrepancy factor ($R \sim 5\%$) for the experimental and theoretically calculated intensities of nuclear and magnetic reflections is achieved when the nickel and lithium atoms are randomly arranged in the cationic sublattice with an occupancy of 1, and the site occupancy of oxygen sublattice is equal to $1 - x$ (Fig. 5). Similar calculations carried out for the $(Ni_{1-x}Mg_x)O$ solid solutions studied earlier in [8] demonstrate that the oxygen site occupancy of the anionic sublattice is equal to 1. From these facts, it can be concluded that, in this case, there are no errors brought about by the method of processing the neutron diffraction patterns; in other words, we deal with the physical result. This suggests that the anionic sublattice in the $(Ni_{1-x}Li_x)O$ solid solutions is characterized by the presence of oxygen vacancies whose concentration corresponds to the lithium concentration.

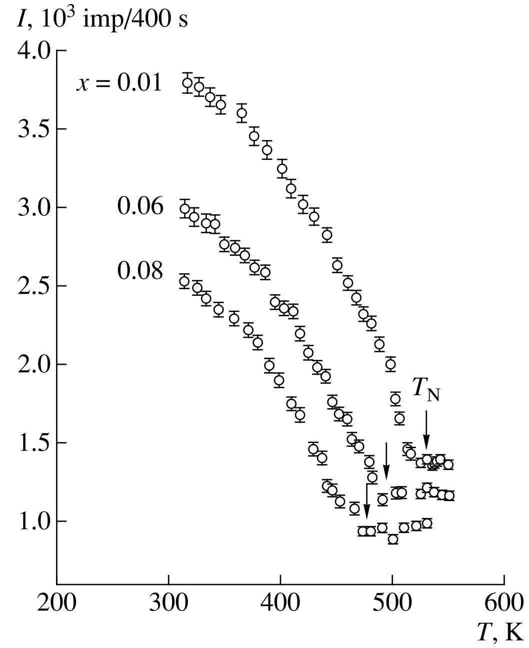

Fig. 3. Temperature dependences of the intensity of the (1/2 1/2 1/2) reflection for the $(Ni_{1-x}Li_x)O$ solid solutions. Arrows indicate the Néel temperatures.

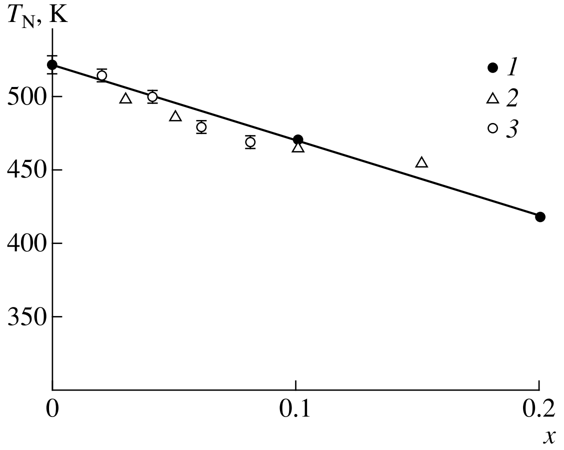

Fig. 4. Concentration dependences of the Néel temperature for the $(Ni_{1-x}Mg_x)O$ and $(Ni_{1-x}Li_x)O$ solid solutions according to the data taken from (*1*) [9], (*2*) [17], and (*3*) this work.

The result obtained was thoroughly analyzed and checked. First of all, we considered two alternative model structures of the $(Ni_{1-x}Li_x)O$ solid solutions. The first model corresponded to the formula $(Ni^{2+}_{1-2x}Ni^{3+}_x Li^{+}_x)O^{2-}$. This implies that the cationic sublattice is completely occupied by the nickel and lithium

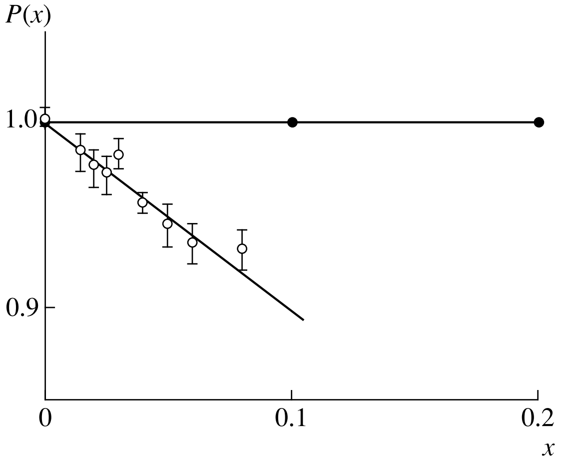

Fig. 5. Oxygen site occupancies of anionic sublattices in the $(Ni_{1-x}Mg_x)O$ (filled circles) and $(Ni_{1-x}Li_x)O$ (open circles) solid solutions. The data are obtained by the fitting of experimental and theoretical intensities with the Rietveld method included in the FULLPROF program.

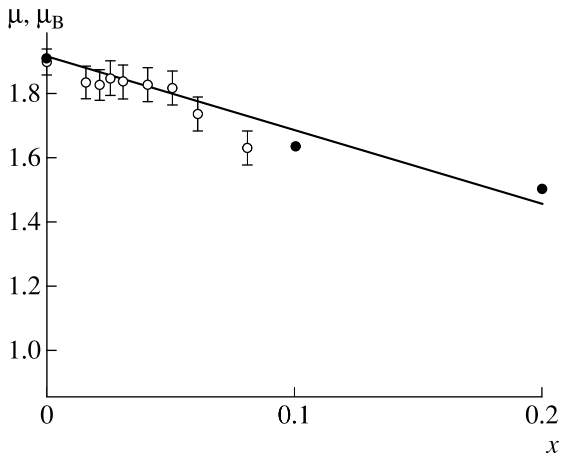

Fig. 6. Concentration dependences of the mean magnetic moment per metal ion in the $(Ni_{1-x}Mg_x)O$ (filled circles) and $(Ni_{1-x}Li_x)O$ (open circles) solid solutions according to the neutron diffraction data obtained in [8] and this work, respectively.

ions, and the anionic sublattice is fully filled by the oxygen ions. The second model was based on the assumption that neutral lithium atoms occupy the tetrahedral sites in the face-centered cubic lattice of oxygen, and the octahedral sites are occupied only by the Ni^{2+} ions. As follows from the calculations performed, in both cases, the discrepancy factors for the experimental and calculated intensities of nuclear reflections are higher than 50%, which indicates the inconsistency of the above models for describing the structural state of lithium atoms in NiO.

In order to obtain further evidence for the defectiveness of the anionic sublattice, the experimental ratios between the integrated intensities of the (111) and (200) nuclear reflections were determined by the independent method (without numerical calculations within the FULLPROF program package). Then, the same ratios were theoretically calculated under the assumption that the oxygen site occupancy P_O of the anionic sublattice is equal to 1 and $1 - x$. The data obtained are summarized in the table. As is seen from the table, the calculated and experimental data are in reasonable agreement when the occupancy of the oxygen sites is equal to $1 - x$. In this case, the intensity ratio $I_{(111)}/I_{(200)}$ is approximately constant over the entire range of compositions, whereas, if the occupancy of the oxygen sublattice is equal to 1, this ratio changes by a factor of about 1.5. Consequently, the inference drawn from the data on the neutron diffraction measurements that the oxygen sublattice in lithium-doped nickel monoxides is imperfect seems to be quite justified.

Experimental and calculated relative intensities of the (111) and (200) reflections for the $(Ni_{1-x}Li_x)O$ solid solutions of different compositions

Concentration	Scattering amplitude	$I_{(111)}/I_{(200)}$		
x	$\langle b \rangle$ 10^{-12} cm	observed	calculated at $P_O = (1 - x)$	calculated at $P_O = 1$
0.010	1.020	0.127	0.139	0.132
0.015	1.012	0.135	0.136	0.128
0.020	1.005	0.133	0.137	0.126
0.025	0.999	0.132	0.136	0.123
0.030	0.994	0.139	0.137	0.121
0.040	0.981	0.133	0.135	0.113
0.050	0.968	0.127	0.129	0.110
0.060	0.809	0.133	0.132	0.105
0.080	0.956	0.136	0.135	0.095

Furthermore, the full-profile analysis of neutron diffraction reflections taken from the powder samples enabled us to determine the concentration dependences of the mean magnetic moment per atom $\mu(x)$ and the unit cell parameter $a(x)$, which are displayed in Figs. 6 and 7, respectively. It can be seen from Fig. 6 that the mean magnetic moment $\langle \mu(x) \rangle$ exhibits a linear behavior similar to that observed for the $(Ni_{1-x}Mg_x)O$ solid solutions. At the same time, the unit cell parameters are close to those determined by the X-ray diffraction analysis and somewhat deviate from the dependence $a(x)$ obtained in [12].

3. DISCUSSION

The experimental data obtained permit us to conclude that lithium-doped nickel monoxides are the substitutional solid solutions, in which the lithium atoms are randomly distributed over the completely occupied cationic sublattice, and the oxygen vacancies with the same concentration are formed in the anionic sublattice. Then, the chemical formula of these solutions should be written as $\mathrm{Ni}^{2+}_{1-x}\mathrm{Li}_x\mathrm{O}^{2-}_{1-x}\square_x$, where $\square$ designates the oxygen vacancy in the anionic sublattice. As follows from this formula, the number of valence electrons of nickel and oxygen ions in lithium-doped NiO remains the same as in undoped NiO. It should be noted that the lithium atoms, which are randomly arranged in the cationic sublattice, are in the neutral state and do not form chemical bonds with oxygen atoms. However, it can be assumed that an outer-shell valence electron of lithium that is described by the wavefunction with the 2*p* symmetry and weakly interacts with the ionic core can be spatially polarized toward an oxygen vacancy. One can also expect the formation of *F*-centers in the anionic sublattice whose concentration corresponds to the concentration of lithium atoms in the solid solution.

We also believe that the low value of electronic work function in these materials can be directly associated with the presence of oxygen vacancies in the anionic sublattice. From the viewpoint of electronic structure, this means that, in defect crystals, the Fermi surface in some points of the reciprocal space is very closely adjacent to the crystal surface. On the other hand, the high hole-type conductivity of lithium-doped nickel monoxides, as compared to the conductivity of the undoped compound, is likely brought about by the formation of an acceptor level induced by doped lithium atoms in the forbidden energy band.

As regards the magnetic properties of lithium-doped nickel monoxides, it should be mentioned that, in the composition range with $x < 0.1$, the compounds remain antiferromagnetic with the same type of magnetic ordering as in undoped nickel monoxide. Note that the substitution of the diamagnetic lithium atom for the magnetic Ni^{2+} ion leads to a linear change in the Néel temperature according to the relationship $T_\mathrm{N} = T_\mathrm{N}^\mathrm{NiO}(1 - x)$, where $x < 0.25$. This is consistent with the conclusion of the molecular-field theory considered in [8, 9] for the substitution of the diamagnetic Mg^{2+} ion for the magnetic Ni^{2+} ion. Therefore, in the composition range under consideration, there are no considerable differences in the diamagnetic dilution with magnesium and lithium. This is also evidenced by similar concentration dependences of the mean magnetic moment per atom, which can be also described by the linear law in this composition range: $\langle\mu\rangle = \mu_\mathrm{Ni}(1 - x) - M_x$, where $\mu_\mathrm{Ni} = 1.9\mu_\mathrm{B}$ is the local magnetic moment at the nickel atoms in the diamagnetically diluted and undiluted NiO, and M_x is the moment induced at the diamagnetic dopant with the direction opposite to the magnetization of the antiferromagnetic sublattice [9].

The similarity in the magnetic properties of the $(\mathrm{Ni}_{1-x}\mathrm{Li}_x)\mathrm{O}$ and $(\mathrm{Ni}_{1-x}\mathrm{Mg}_x)\mathrm{O}$ solid solutions in the composition range $0 \le x < 0.1$ primarily suggests that the exchange interaction between the magnetic nickel ions occurs within the cationic sublattices, which show identical behavior in both systems. In solid solutions of both types, the main parameters of the magnetic subsystem are the exchange integrals $J_1 > 0$, $J_2 < 0$, and $J_3 > 0$ at distances of the first ($r_1 = \frac{\sqrt{2}}{2}a$), second ($r_2 = a$), and third ($r_3 = \sqrt{3}\,a$) nearest neighbors, respectively. This character of the exchange interaction is accomplished solely in solid solutions with the NaCl-type crystal lattice, which, in the $(\mathrm{Ni}_{1-x}\mathrm{Li}_x)\mathrm{O}$ system, is observed only to $x = 0.5$. Then, there occurs the structural transformation from the cubic phase to the NiLiO_2 hexagonal phase. The latter phase is characterized by the ordered arrangement of lithium and nickel atoms and also by the ferromagnetic spin ordering. Note that the NiLiO_2-type short-range order elements appear already at $x = 0.3$. As a result, in the composition range $0.3 < x < 0.5$, as the diamagnetic atoms occupy one of the antiferromagnetic sublattices, its magnetization becomes less than the magnetization of another sublattice. This gives rise to the ferrimagnetic structure associated with the uncompensated antiferromagnetic sublattices.

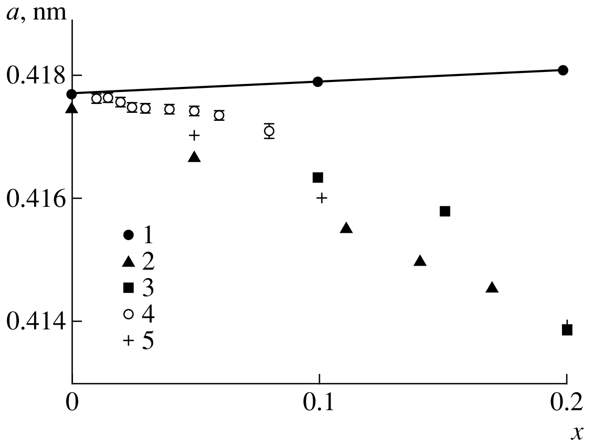

Fig. 7. Concentration dependences of the unit cell parameter for the $(\mathrm{Ni}_{1-x}\mathrm{Li}_x)\mathrm{O}$ and $(\mathrm{Ni}_{1-x}\mathrm{Mg}_x)\mathrm{O}$ solid solutions according to the data taken from (*1*) [8], (*2*) [10], (*3*) [13], (*4*) this work, and (*5*) [12].

The main experimental result of the present neutron diffraction investigation is the revelation of the defectiveness of the oxygen sublattice in lithium-doped NiO. This result could be achieved only with the optimum ratio between the nuclear-scattering amplitudes of lithium, nickel, and oxygen atoms. It is not improbable that the revelation of the defectiveness of the oxygen sublattice in the lithium-doped nickel monoxide will provide an explanation for the specific features of electrical properties of these materials that manifest themselves in the high electrical conductivity and a low value of the electronic work function.

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